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Thin nitrogen-containing titanium coatings formed on the PLLA scaffolds surface by reactive magnetron sputtering

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Abstract. This paper describes the possibility of using a mixture of nitrogen (N_2) and xenon (Xe) at different volume concentration for bioresorbable electrospun poly-(l-lactic) acid (PLLA) scaffolds surface modification by reactive DC magnetron sputtering of a titanium target. It was observed that the selected technological modes do not reliably affect the morphology of scaffolds and simultaneously, increased their hydrophilicity. Moreover, the results of the X-ray photoelectron spectroscopic investigation show that the composition of the thin film coating consists mainly of compounds of titanium oxides (Ti_xO_y) and titanium oxynitrides (TiO_xN_y) and slightly depend of gas ratio. In another hand, C-O and C=O ratio depends of concentration of Xe and decreases with its increasing.
Keywords: electrospun PLLA scaffold; reactive magnetron sputtering; gases mixture; nitrogen-containing titanium coating; biomedical material.

1. Introduction

Poly-L-lactic acid (PLLA) polymer [1] is widely used for the production of bioresorbable scaffolds due to their high physicochemical and strength characteristics, as well as a variety of processing methods. Among the many processing methods, the most common is the electrospinning method [2]. High strength, significant relative elongation of scaffolds formed by the electrospinning method from PLLA allows their wide application in the field of tissue engineering. However, their use for applications in this field is limited by the high hydrophobicity of the surface, which prevents cell adhesion and proliferation.

Nowadays, plasma deposed thin nitrogen-containing titanium coatings (TiN_xO_y) are increasingly being used in the medical field because the properties of TiN_xO_y coatings can be controlled by their own structure and chemical composition [3].

Reactive magnetron sputtering is the most versatile method of TiN_xO_y coatings deposition because it allows to vary the process parameters within a wide range. It is known that the working gas has a strong influence on the chemical properties of the formed coatings [4]. Therefore, the use of reactive and inert gases as well as their mixtures has become common for the formation of various TiNxOy coatings. Varying the composition and ratio of the working gases, it is possible to carry out not only the "soft" treatment of the bioresorbable PLLA scaffolds, on the chemical composition of the formed coatings. On the other hand, there are no studies in the scientific literature devoted to the influence of the N_2/Xe mixture concentration on the chemical composition of the titanium nitrogen-containing coatings formed on the surface of bioresorbable PLLA scaffolds.

This paper studies the possibility of forming a nitrogen-containing titanium coating to modify the surface of electrospun PLLA scaffolds using a DC magnetron discharge plasma operating in a mixture of nitrogen and xenon working gas in various volume ratio. Surface-modified polymer scaffolds were investigated in terms of morphology and physicochemical properties.

2. Materials and methods

Polymeric fibrous scaffolds formed from 3 wt.% spinning solution poly-L-lactic acid (PLLA; PL-18, Corbian – Purac Biochem BV, Netherlands) in chloroform ($CHCl_3$; purchased from EKROS, Russia) were used. A commercially available electrospinning device (NANON-01A, MECC Co., Japan) was used to fabricate the polymer scaffolds, applying the following electrospinning parameters: distance between nozzle and counter electrode 110 mm, spinning solution flow rate 4 mL/h, voltage 22 kV. The produced scaffolds were exposed to a vacuum of 10^{-2} Pa at a temperature of 100 °C for 10 hours to remove the residual $CHCl_3$ before the process of modifying takes place.

The deposition of titanium nitrogen-containing coatings was carried out by reactive direct current (DC) magnetron sputtering of a solid titanium target (99.99%) in an atmosphere of nitrogen (N_2, 99.999%, Metal Bureau, Russia) with xenon mixture (Xe, 99.9995%, PTK Cryogen, Russia) at different volume concentrations: N_2 100 (Xe:N_2 = 0:100), Xe75/$N_2$25 (Xe:N_2 = 75:25), Xe50/$N_2$50 (Xe:N_2 = 50:50), Xe25/$N_2$75 (Xe:N_2 = 25:75) and Xe100 (Xe:N_2 = 100:0). Universal magnetron sputtering system utilized for coating deposition is described in the following reference [5]. The following technological parameters were used to form coatings: distance between the target and the sample 33 mm, reliminary pressure in the magnetron chamber 3×10^{-3} Pa, working pressure in the magnetron chamber 0.8 Pa. The area of the sputtered target was 224 cm^2. The plasma treatment was carried out for 2 minutes at a power of 88 W. The modification was carried out in a cyclic mode to reduce the destruction of the polymer sample under the influence of plasma as follows: 1 minute of plasma modification, at a break of 3 minutes.

PLLA scaffolds surface topology was studied using atomic force microscopy (AFM) (NSG01, NT-MDT, Russia) in air at the semicontact mode. Results were processed in Gwyddion program.

Surface characterization were carried out using X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, USA) with AlKα radiation (photon energy is 1486.6 eV). The total energy resolution of the experiments performed were 0.3 eV. XPS Spectra were recorded in the constant pass energy mode (50 eV for survey spectrum and 20 eV for element core level spectrum) using XPS spot size of 650 µm in diameter. Investigations were carried out at room temperature in ultra-high vacuum (UHV) with a pressure in the order of 1×10^{-9} mbar. N1s, C1s, O1s and Ti2p spectra were deconvoluted utilizing the Voigt function in OriginPro 9.0 software.

Wettability investigations of the PLLA scaffolds were carried out on an KRÜSS Easy Drop DSA 20 instrument (Krüss, Germany) performing the sessile drop method by measuring the contact angle. To characterize differences in the contact angle of electrospun PLLA scaffolds, glycerol, a highly viscous polar liquid, was used with a volume of 3 µL placed on the sample surface. The glycerol contact angles were one minute after the glycerol droplet was placed on the sample surface.

Statistical processing of the obtained results was carried out using Statistica 7.0 (StatSoft, Tulsa, USA). Most data are presented as mean ± standard deviation. Differences were considered statistically significant at $p < 0.05$. The significance of these differences were determined using the one-way ANOVA test.

3. Results

In Fig.1, the AFM images of PLLA scaffolds modified in a mixture of nitrogen with xenon at different volume concentrations are shown.

As can be seen from the AFM images, PLLA scaffolds morphology is a fibrous structure in which the fibers are chaotically intermingled with each other. The fibers have an irregular shape with a mean diameter in the range of 1.4–1.6 ± 0.4 µm. Defects in the form of melting and burning are not observed on the surface of the fibers.

Fig.2 shows the Ti2p, O1s, N1s, C1s XPS spectra of the PLLA scaffolds modify in a mixture of nitrogen with xenon at different volume concentrations.

The Ti 2p spectrum for the untreated PLLA scaffold sample (Fig.2a) shows no reflexes of titanium and its compounds. After plasma treatment, a doublet at 458.5 and 464.2 eV is observed in the spectrum, which corresponds to the Ti 2p3/2 and Ti 2p1/2 electronic states and a satellite at

471.6 eV for all volume concentrations. The presence of the observed reflexes characterizes the oxidation degree of Ti^{4+} in TiO_2 and the presence of a complex Ti-O-N bond.

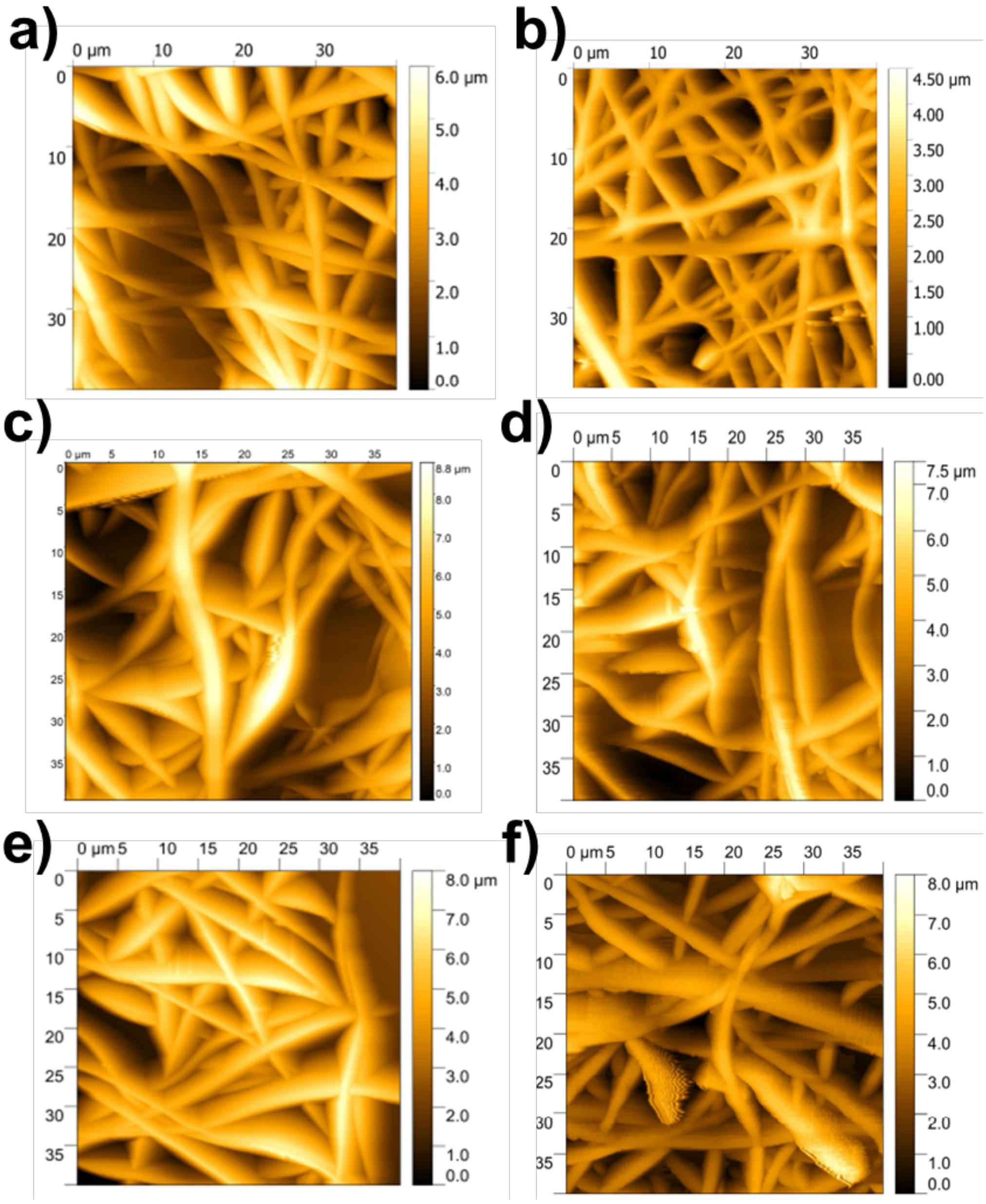

Fig.1. AFM images of PLLA scaffolds modified in a mixture of nitrogen with xenon at different volume concentrations: a) control (unmodified PLLA scaffold), b) $Xe:N_2$ = 0:100, c) $Xe:N_2$ = 75:25, d) $Xe:N_2$ = 50:50, e) $Xe:N_2$ = 25:75, f) $Xe:N_2$ = 100:0.

In the O 1s spectrum for the untreated PLLA scaffold sample (Fig.2b), two reflexes at 532.2 and 531.1 eV are observed, corresponding to the C=O and C-O bonds in PLLA main polymeric chain. After plasma treatment for either volume concentrations of gases mixtures a shift of the reflex toward lower bond energy is observed, indicating the destruction of the C=O double bond. In addition, after plasma treatment, the formation of an intense shoulder at 530.0 eV bond energy is observed, which corresponds to Ti-O or Ti-O-N chemical bonds and characterizes the O_2^- ion in the TiO_2 lattice. In the region of 530.5 to 534.5 eV a broad shoulder is observed in which a reflex can be distinguished at a bond energy of 531.5 eV, which corresponds to a complex Ti-O-N bond [6]. It is also worth noting the decrease in the relative intensity of the C-O peak with increasing Xe concentration in the gases mixture.

In the N 1s electron spectrum of the untreated scaffold, there are no reflexes characteristic of nitrogen (Fig.2c) and its compounds. After plasma modification, the spectrum shows a wide reflection with a maximum in the region of 399.6 eV, which characterizes the presence of Ti-O-N bonds in the coating. Also in the region of 402–400 eV a broad shoulder can be distinguished, which is characteristic of NH_3^- and O=C-NH compounds.

In the 1S spectrum of the carbon atom (Fig.2d) for the untreated scaffold, three main reflexes was observed 289.2 eV (C=O/O-C=O), 286.8 eV (C-OH/C-O-C) and 284.8 eV (C-H/C-C). These compounds are characterizing the main chemical bonds in PLLA [7]. After plasma modification the reflex intensity in the 289.2 eV region decreases significantly, which is indirect evidence for the formation of Ti-O-N on the PLLA scaffolds surface.

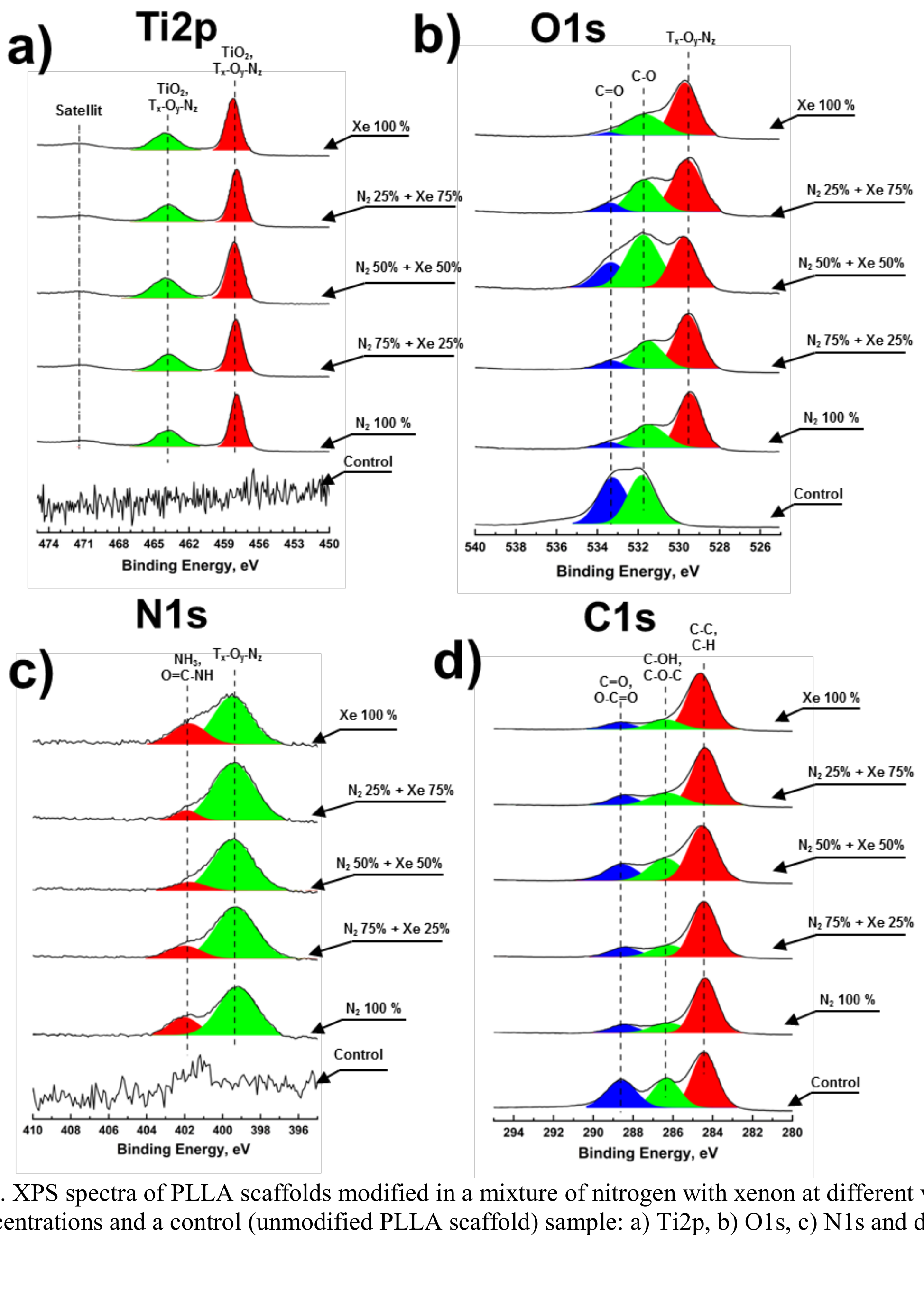

Fig.2. XPS spectra of PLLA scaffolds modified in a mixture of nitrogen with xenon at different volume concentrations and a control (unmodified PLLA scaffold) sample: a) Ti2p, b) O1s, c) N1s and d) C1s.

Results of the wettability investigation of the PLLA scaffolds after one minute contact with glycerol are presented in Fig.3.

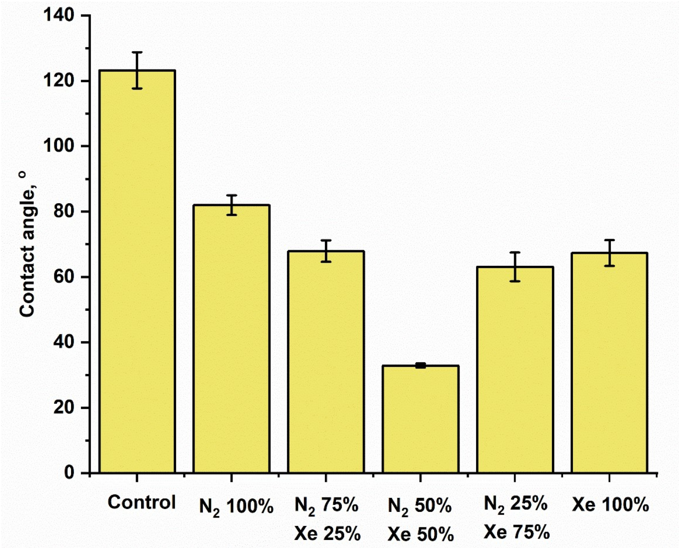

Fig.3. Glycerol contact angle (GCA) of PLLA scaffolds modified in a mixture of nitrogen with xenon at different volume concentrations and a control (unmodified PLLA scaffold) sample.

4. Conclusion

Thus, the paper shows the possibility of using a mixture of nitrogen (N_2) and xenon (Xe) at different volume concentration to modify PLLA scaffolds formed by electrospinning in reactive DC magnetron discharge plasma arising from the sputtering of a titanium target. It was found that the selected technological parameters do not reliably change the morphology of the scaffolds, while allowing to give their surface low glycerol contact angle that minimal for Xe:N_2 = 50:50 ratio and equal 33° ± 6°. X-ray photoelectron spectroscopic investigation show that the composition of the thin film coating consists mainly of compounds of titanium oxides (Ti_xO_y) and titanium oxynitrides (TiO_xN_y) and slightly depend of gas ratio. In another hand, C-O and C=O ratio depends of concentration of Xe and decreases with its increasing.

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5. References

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